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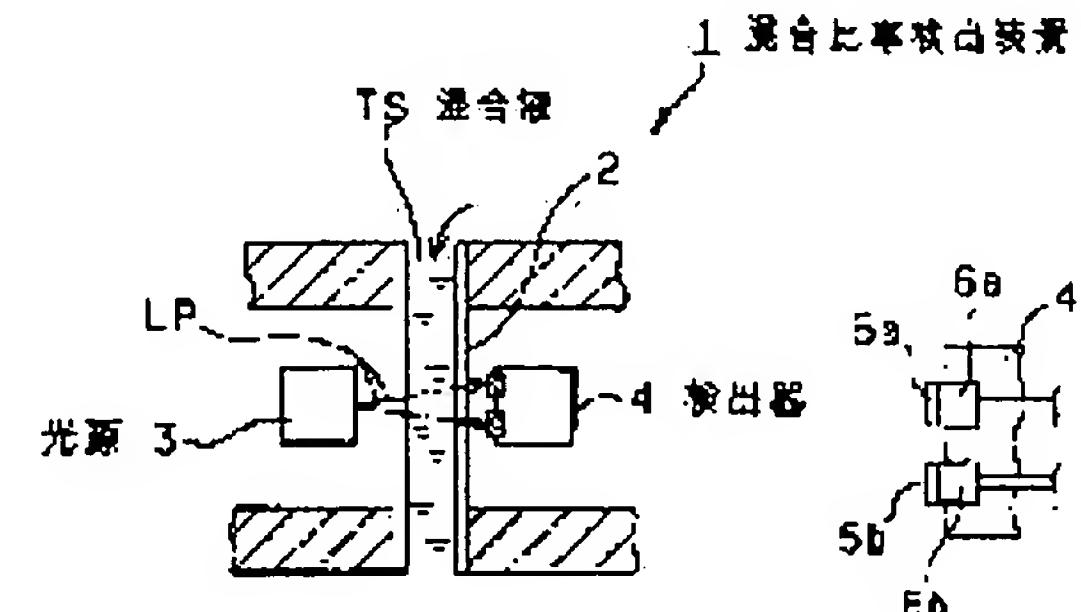
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(54) METHOD FOR DETECTING ALCOHOL/WATER MIXING RATIO AND DEVICE FOR DETECTING ALCOHOL/WATER MIXING RATIO

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a method and device for detecting alcohol/water mixing ratio hardly influenced by the measuring environment and capable of doing precise measurement.

SOLUTION: This device comprises a light source 3 for emitting a light in infrared area and a detector 4 for detecting the light in infrared area from the light source 3. An optical path LP between the light source 3 and the detector 4 is passed to an alcohol/water mixture TS, the infrared absorption quantity by the alcohol or water contained in the alcohol/water mixture TS is detected, and the mixing ratio is determined on the basis of the detection result.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the mixing ratio detection sensor of the alcohol/water used for a fuel cell etc., for example.

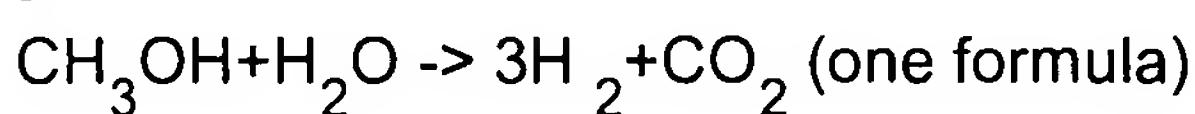
[0002]

[Description of the Prior Art] Now, development of the solid polymer type fuel cell of the low-temperature operation type expected as new energy sources, such as an electromobile, is furthered. Pure water matter, methanol (methanol-reforming gas is also included), hydrogen by the partial oxidation of gasoline, etc. are thought as a fuel-supply method to such a fuel cell.

[0003] From environment or an efficiency side, it excels in order of gasoline < methanol < pure water matter, and becomes the order of pure water matter < methanol < gasoline from the ease of carrying out of correspondence of another side and an equipment surface (infrastructure), and it is concluded for [, such as a car,] mobiles that use of methanol is in use.

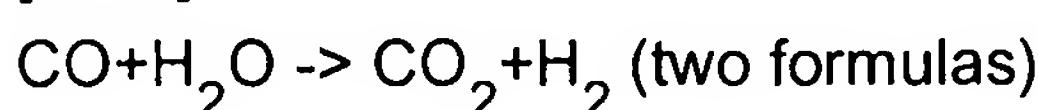
[0004] the steam reforming reaction which makes hydrogen using methanol generate -- 75% of H_2 , and 25% of CO_2 -- theoretical -- generating (one formula) -- although it is **, unreacted methanol, a small amount of carbon monoxide (CO), etc. are contained.

[0005]



This CO has the poisoning operation to the catalyst of the polar zone, and in order to reduce battery capacity, it needs to convert CO into CO_2 by a water gas shift reaction (two formulas).

[0006]



For this reason, methanol and water which are introduced into a reformer need to be the presentation of a predetermined rate with more water than 1:1 in a mole ratio. Control of the mixing ratio of this methanol and water is dramatically important.

[0007] Although a fuel cell is not related, it is measurement also with important detection of the manufacturing process of alcoholic content drinks, such as Japanese sake and white distilled liquor, or the mixing ratio of

the ethanol/water in an inspection.

[0008]

[Problem(s) to be Solved by the Invention] In measurement of the mixing ratio of methanol and water in conventional technology, what detects the specific gravity of mixed liquor exists.

[0009] For example, in a fuel cell, what is indicated to JP,8-91804,A has arranged the sensor in a reservoir, and has judged the mixing ratio by detecting the specific gravity and temperature of mixed liquor and amending a measurement-of-specific-gravity value according to temperature.

[0010] However, the measurement by the specific gravity difference of the above-mentioned methanol and water becomes difficult [it / to maintain accuracy from it being necessary to contact a sensor, a sensing device, and the mixed liquor itself directly to the measurement under the environment where it is vibrating, and measurement, in the state where there is a flow].

[0011] Even if measurement environment and conditions are good, in sensor composition provided with the portion accompanied by mechanical ****, such as a floating body, it is difficult to raise more the accuracy of measurement of measurement of specific gravity.

[0012] This invention solves the problem of the above-mentioned conventional technology. The purpose is to provide the mixing ratio detecting method and device of alcohol/water which enable highly precise measurement that it is hard to be influenced by measurement environment.

[0013] In this explanation, although it shall use as what includes ethanol, methanol, etc., methanol is explained to be alcohol below as one of the suitable examples of an object.

[0014]

[Means for Solving the Problem] To achieve the above objects, if it is in a mixing ratio detecting method of the alcohol/water of this invention, A detecting method detected via a filter means which has a window of a penetration in a wavelength band region where infrared extinction according light of an infrared region which made inside of mixed liquor of alcohol/water penetrate, and penetrated light of an infrared region to alcohol or water is performed, It applies to two or more mixed liquor of the alcohol/water of the mixing ratio which the mixing ratio has become clear beforehand and is different, Correlation of the mixing ratio and a detection result is searched for, and the mixing ratio of mixed liquor of the alcohol/water which serves as a measuring object based on said correlation is searched for from a detection result obtained by applying said detecting method to mixed liquor of the alcohol/water used as a measuring object.

[0015] If it is in a mixing ratio sensing device of alcohol/water, A light source which generates light of an infrared region including a wavelength band region which infrared extinction by alcohol or water generates, It has a window of a penetration in a wavelength band region where infrared extinction by alcohol or water is performed in a detection means to detect light of an infrared region from said light source, and light of an infrared region, It has a filter means arranged before said detection means, and it provides so that it may pass through inside of mixed liquor of the alcohol/water which serves as a measuring object in an optical path of light of an infrared region between said light source and a detection means.

[0016] By being constituted in this way, light of an infrared region passes through inside of mixed liquor of the alcohol/water used as a measuring object, and it becomes detectable by filter means and a detection means about an infrared absorption which changes according to the mixing ratio of alcohol/water.

[0017]It is also preferred that mixed liquor of the alcohol/water used as a measuring object passes an inside of a container via a transmission window part which has arranged said light source, a detection means, and a filter means besides said container and with which was provided with a container supplied to an inside, and a container was equipped in an optical path of said light.

[0018]It can measure without contacting mixed liquor to the device itself, and improvement in operation stability and maintenance nature is achieved.

[0019]The mixing ratio and a memory measure holding information on correlation of a detection result which are acquired based on a detection result obtained two or more mixed liquor [for] of the alcohol/water of the mixing ratio which the mixing ratio has become clear beforehand and is different, It is also preferred to calculate a detection result of mixed liquor of the alcohol/water used as a measuring object based on information on correlation held at said memory measure, to search for the mixing ratio of mixed liquor of the alcohol/water used as a measuring object, and to have an arithmetic output means to output.

[0020]Thus, by having a memory measure and an arithmetic output means, error correction of a detection result by individual difference of a device is performed, and improvement in detecting accuracy is achieved.

[0021]In [it is arranged in the middle of an optical path between said light source and a detection means, and] light of an infrared region, The 2nd filter means that has a window of a penetration in a wavelength band region except a wavelength band region where infrared absorption by alcohol or water is performed, It has the 2nd detection means that detects light of an infrared region which passed said 2nd filter means, and it is also preferred for said arithmetic output means to use a differential output of two detection means of said detection means and the 2nd detection means as a detection result of mixed liquor of the alcohol/water used as a measuring object.

[0022]Since a reference output which is not related to a concentration state of mixed liquor of alcohol/water can be obtained by the 2nd filter means and the 2nd detection means and change of a delicate detect output of alcohol or water is made into a differential output with a reference output, Highly precise detection for which it does not depend on measurement environment more can be performed.

[0023]It is also preferred to have a light reflector which makes said optical path crooked.

[0024]Flexibility on an equipment configuration or arrangement can be raised and it can be considered as arrangement configurations which influence cannot receive easily, such as a miniaturization and vibration.

[0025]With a wavelength band region where infrared extinction by alcohol or water is performed in light of an infrared region. They are either 2.2 micrometers - 2.4 micrometers, 3.2 micrometers - 3.6 micrometers, 6.4 micrometers - 7.3 micrometers, and 8.5 micrometers - 10.5 micrometers as a wavelength band region where infrared extinction of alcohol is performed, It is preferred that they are also either 1.3 micrometers - 1.6 micrometers, 1.7 micrometers - 2.2 micrometers, 2.6 micrometers - 3.4 micrometers, and 5.5 micrometers - 6.5 micrometers as a wavelength band region where infrared extinction of water is performed.

[0026]

[Embodiment of the Invention]With reference to drawings, the composition of the mixing ratio sensing device of alcohol/water and the mixing ratio detecting method of alcohol/water are explained below. Here, methanol, ethanol, etc. shall be included with alcohol.

[0027]In the mixing ratio sensing device 1 (it is hereafter called a mixing ratio sensing device) of the alcohol/water shown in drawing 1. The light source 3 which generates the light of an infrared region on both

sides of the pipe 2 which penetrates the infrared light as a container with which mixed liquor TS (it is hereafter called mixed liquor) of the alcohol/water used as a measuring object is supplied to an inside, and the detector 4 as a detection means to detect the light of an infrared region are arranged. LP gas is an optical path between the light source 3 and the detector 4.

[0028]Although the whole pipe is used as the material which penetrates infrared light by this embodiment as the pipe 2, it is possible to have composition which equips with a transmission window part the portion which optical-path LP gas passes.

[0029]The detector 4 is equipped with the infrared photo detectors 6a and 6b which receive two infrared light, The infrared photo detector 6a is equipped with the filter 5a as a filter means which has a window of a penetration in the wavelength band region where infrared absorption by alcohol or water is performed, The infrared photo detector 6b is equipped with the filter 5b as the 2nd filter means that has a window of a penetration in the zone except the wavelength band region where infrared absorption by alcohol or water is performed.

[0030]Each filters 5a and 5b are arranged in the middle of optical-path LP gas between the light source 3 and the infrared photo detectors 6a and 6b of the detector 4.

[0031]The wavelength band region where infrared absorption by alcohol is performed is a wavelength band region of either 2.2 micrometers - 2.4 micrometers (2.3-micrometer belt), 3.2 micrometers - 3.6 micrometers (3.5-micrometer belt), 6.4 micrometers - 7.3 micrometers (6.9-micrometer belt), and 8.5 micrometers - 10.5 micrometers (9.5-micrometer belt).

[0032]The wavelength band regions where infrared absorption by water is performed are either 1.3 micrometers - 1.6 micrometers (1.4-micrometer belt), 1.7 micrometers - 2.2 micrometers (1.9-micrometer belt), 2.6 micrometers - 3.4 micrometers (3.0-micrometer belt), and 5.5 micrometers - 6.5 micrometers (6.0-micrometer belt).

[0033]It is satisfactory also as a filter as for which the 3.0(2.6-3.4)μm belt which is especially a water absorption belt has a window of a 2.5-7-micrometer penetration since the zone with large absorption intensity is large (the influence of absorption of the 3.5-micrometer belt of alcohol is small).

[0034]Since the absorption intensity of the 1.4-micrometer (1.3-micrometer - 1.6 micrometers) belt which is a water absorption belt is also large, it is satisfactory also as a filter with the window of a penetration of light region -7micrometer (the influence of absorption of the 2.3-micrometer belt of alcohol is also small).

[0035]Be [what is necessary / just although the infrared light (infrared rays) up to -11micrometer comes out at least since the wavelength band region where infrared absorption by alcohol or water is performed as the light source 3 appears comparatively broadly], the lamp etc. which were used for the filament tend to use tungsten etc., for example, being small.

[0036]As the infrared photo detectors 6a and 6b of the detector 4, there are a quantum type photoconducted type sensor and a photoelectromotive-force type sensor, a thermo pile bolometer of a thermal type, a pyroelectric sensor, etc., and all can be adapted. The thermal type is more suitable especially.

[0037]Only the infrared light which passed the filters 5a and 5b, respectively enters into the infrared photo detectors 6a and 6b.

[0038]Such a mixing ratio sensing device 1 of the alcohol/water of composition, In using only the detection result of the infrared photo detector 6a, the specific wavelength band region (for example, when a filter with

the window of the penetration which is 2.5-7 micrometers to which infrared extinction by water is performed is chosen) according to alcohol in mixed liquor TS, and the mixture ratio of water -- according to the absorbed amount of the infrared light in the wavelength band region, It becomes possible to measure the mixing ratio of alcohol/water by the quantity of the infrared light which passes the filter 5a changing, and changing the detect output of the detector 6a.

[0039]In order to measure the mixing ratio of more exact alcohol/water, the mixing ratio has become clear beforehand, And it measures to two or more mixed liquor TS1 of the alcohol/water of the different mixing ratio, TS2, and ..., The correlation of the mixing ratio and a detection result is searched for, the mixing ratio of mixed liquor TS which became a measuring object based on said correlation is calculated from the detection result of mixed liquor TS used as a measuring object, and the method of asking is used.

[0040]It is graph charts showing the absorption to each mixed liquor which drawing 9 added [mixed liquor] 1.5 mol of water, 1.75 mol, and 2.0 mol to alcoholic 1mol, and changed the mixture ratio, and the absorption is changing because the mixture ratio differs.

[0041]drawing 10 -- alcohol and water -- they are each graph charts showing the absorption in the case of independent.

[0042]It is possible to calculate using the function to which the mixing ratio and a detect output are made to correspond to calculate based on correlation, to divide a detect output into an infinitesimal area, to carry out the hold stores of the mixing ratio [/ in the field], and to carry out matrix correspondence, etc.

[0043]Drawing 2 is a figure showing the circuitry which carries out data processing of the detection result from the detector 4, and is considered as the output of the mixing ratio as a block diagram.

[0044]With the data about the correlation of the mixing ratio acquired by the mixed liquor which is memorized by the memory measure 8, and the mixing ratio was proved beforehand that it is, and a detection result, the signal from the detector 4 is inputted into the arithmetic output means 7, and is outputted as the mixing ratio.

[0045]Thus, it has the memory measure 8 and the arithmetic output means 7, and by authorizing the measurement result of each device, error correction of the detection result by the individual difference of a device is performed, and improvement in much more detecting accuracy is achieved.

[0046]In the composition of drawing 1, when accuracy is required more, or when being used at a wide range temperature, it is made to correspond, and it has the 2nd filter 5b and infrared photo detector 6b of a lot further as a reference.

[0047]It is necessary to set up the transmission window of this 2nd filter 5b in addition to the infrared absorption wavelength zone included in alcohol or a water absorption wavelength band region, and object environment. It is usable in what has a window of a penetration in the wavelength band region (visible light - a 1.3-micrometer belt or a 3.7-5.4-micrometer belt, for example, 1.1 micrometers, 4.0 micrometers, or 4.6 micrometers).

[0048]And as shown in drawing 3 in which the circuitry of the detection value processing means was shown in block diagram, the output of two photo detectors of the infrared photo detector 6a and the 2nd infrared photo detector 6b is processed as a differential output.

[0049]By taking the difference signal of the mixed liquor output signal S1 (output value related to the mixing ratio), and the reference output signal S2 in the operating circuit K1, the delicate signal change of the mixed liquor output signal S1 is detected.

[0050]The reference output signal S2 is a thing using not being dependent on the mixing ratio, and this makes this operation output mixed liquor output signal S4 amplified and amended.

[0051]Since the mixed liquor output signal S1 and the reference output signal S2 change relatively about correction for temperature, From it being possible to detect a more exact concentration change by taking difference, therefore, correction for temperature, What is necessary will be to take into consideration only a changed part by the difference in the temperature dependence of some of each output signal, and amendment by the temperature output signal S3 is added to the difference signal of the mixed liquor output signal S1 and the reference output signal S2.

[0052]Thus, a highly precise mixed liquor output signal (amended mixed liquor output signal S4) is acquired at a wide range temperature by having a reference output.

[0053](Referring to drawing 2) and the more exact mixing ratio can be searched for by making this mixed liquor output signal S4 into the output signal of the detector 4.

[0054]Also in the state where mixed liquor TS of the alcohol/water which does not need to carry out direct contact of the sensing device itself to mixed liquor, and serves as a measuring object is vibrating in order to use infrared light, or there is a flow, It can become possible to maintain the accuracy of measurement, and a movable part can be lost as a sensor, and working reliability can be raised.

[0055]Since a measuring object area will be set up by optical-path LP gas, it is also possible to raise the accuracy of measurement more by making optical-path LP gas into two or more, or making it crooked with a light reflector and carrying out multiple-times passage so that it may mention later.

[0056]Drawing 4 and drawing 5 are provided with the light reflector 9 which reflects infrared rays well, are the embodiment which changed the arrangement configuration of the light source 3 and the detector 4, and show the composition of the mixing ratio sensing devices 1B and 1C.

[0057]In drawing 4, it is the composition that arrange the light source 3 and the detector 4 to the same side, and optical-path LP gas passes the pipe 2 twice with the light reflector 9.

[0058]The pipe 2 is supported horizontally, and the end is plugged up and drawing 5 is provided with the two light reflectors 9. Since the fall of the response by the stagnation of mixed liquor TS of the alcohol/water in a detection position is also considered by plugging up an end, the composition of making the both ends of the pipe 2 having a good understanding like drawing 1 and drawing 4 may be used, and it is also good to bend in the shape of a U character, and to make both ends have a good understanding to a container.

[0059]Thus, the light source 3 and the detector 4 are good also as composition which has arranged the light reflectors 9, such as a mirror which may make it counter, arrange to the same side, and reflects infrared rays in an opposite portion efficiently. Arrangement (level, a perpendicular, etc.) and the gestalt of the passage of mixed liquor can be arbitrarily arranged according to a situation.

[0060]Drawing 6, drawing 7, and drawing 8 are beam composition with direct taking about the light source 3 and the detector 4 at the container 12 in the case where mixed liquor TS of the alcohol/water which becomes the container 12 with a measuring object is held.

[0061]Also in this embodiment, the light source 3 and the detector 4 are good also as composition which has arranged the light reflectors 9, such as a mirror which may make it counter, arrange to the same side, and reflects infrared rays in an opposite portion efficiently. Arrangement (level, a perpendicular, etc.) of the passage of mixed liquor can be arbitrarily arranged according to a situation.

[0062]Although not shown by a diagram, a transmission window may be provided in the container 12 and the light source 3 and the detector 4 may be formed in the exterior of the container 12. Also in this case, the light source 3 and the detector 4 are good also as composition which has arranged the light reflectors 9, such as a mirror which may make it correspond, arrange to the same side, and reflects infrared rays in an opposite portion efficiently.

[0063]

[Effect of the Invention]According to this invention explained as mentioned above, it becomes possible to measure the mixing ratio of the mixed liquor of alcohol/water with high precision.

[0064]Also in the state where mixed liquor TS of the alcohol/water used as a measuring object is vibrating, or there is a flow, it can become possible to maintain the accuracy of measurement, and a movable part can be lost, and working reliability can be raised.

[0065]By having a memory measure and an arithmetic output means, error correction of the detection result by the individual difference of a device is performed, and improvement in detecting accuracy is achieved.

[0066]If the 2nd filter means and the 2nd detection means used as a reference are used together, the mixing ratio will become measurable more at a wide range temperature at high degree of accuracy.

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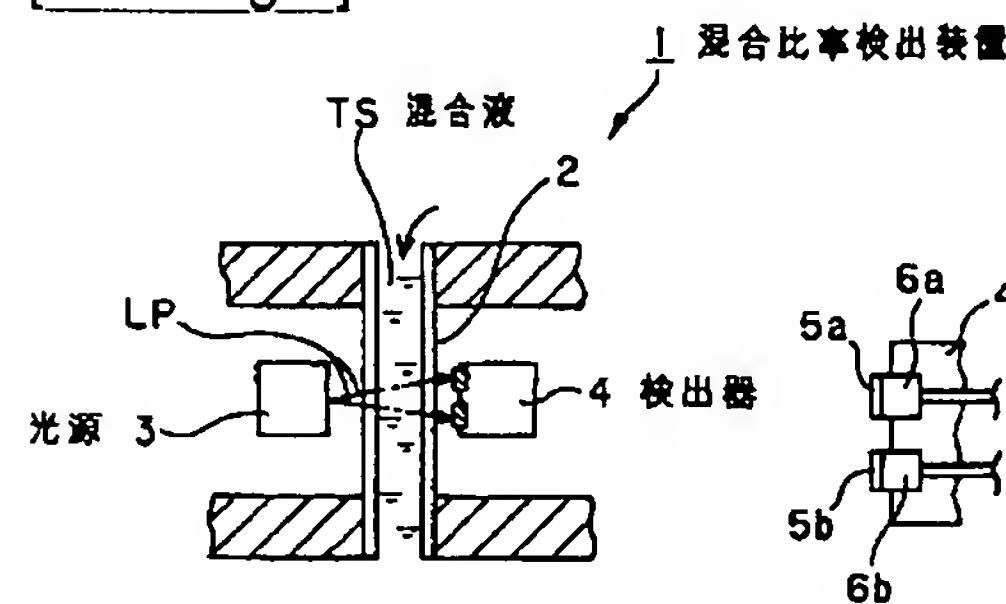
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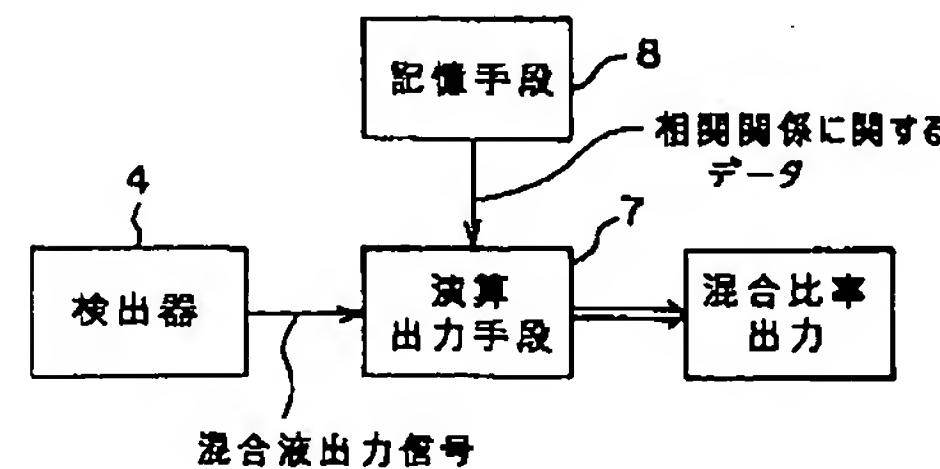
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DRAWINGS

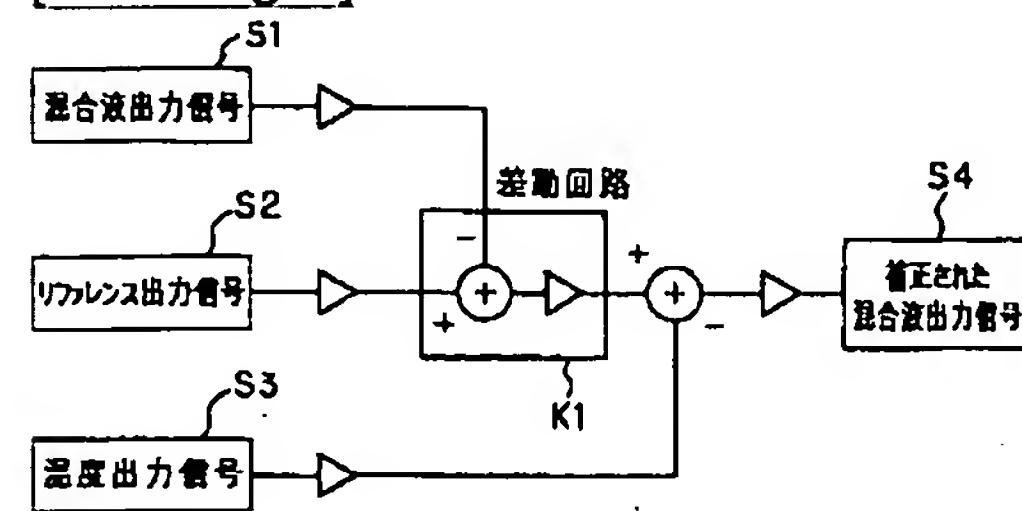
[Drawing 1]



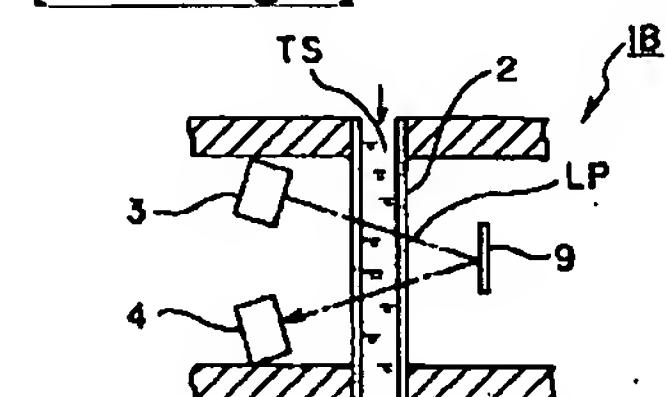
[Drawing 2]

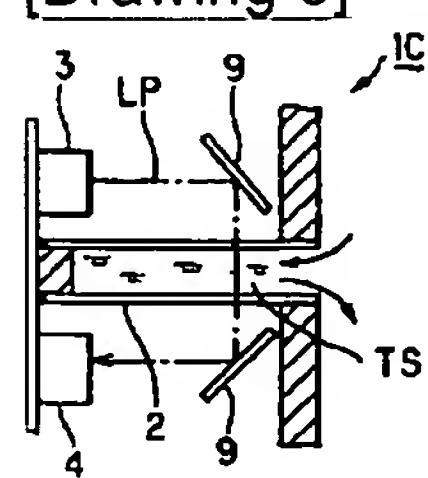
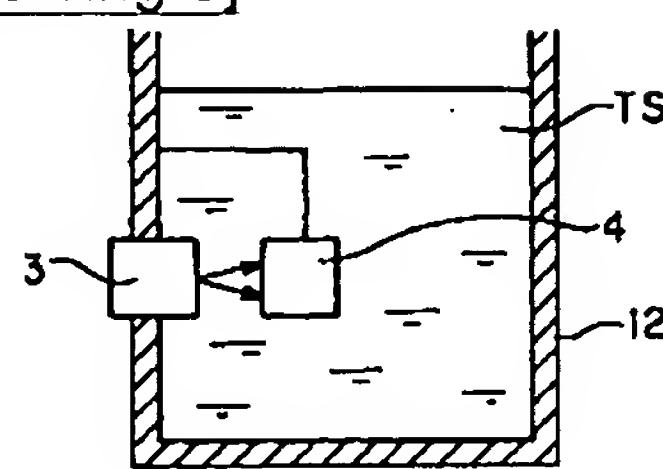
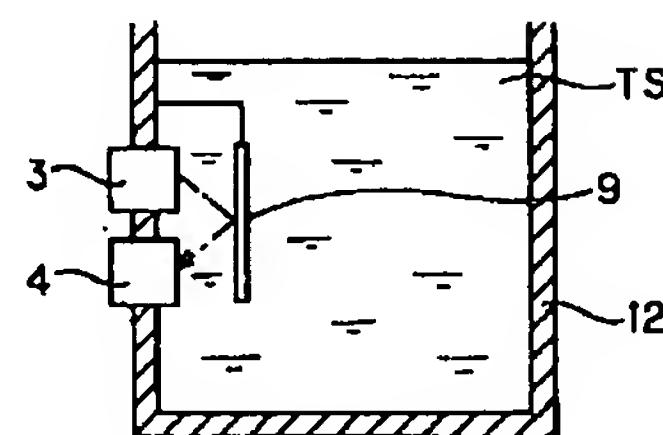
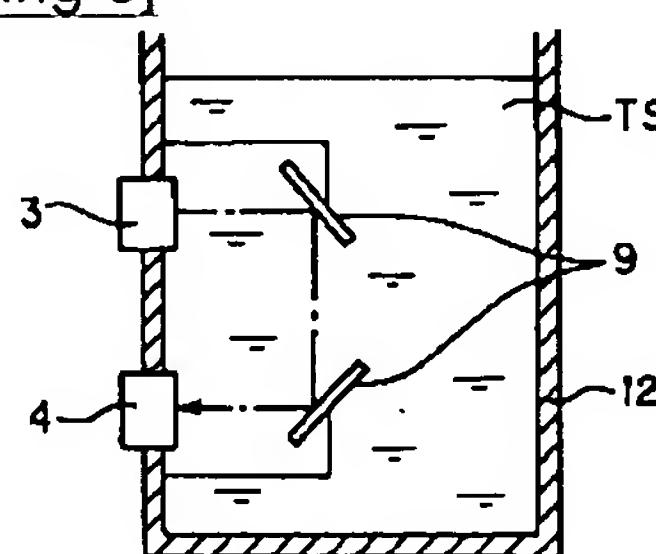
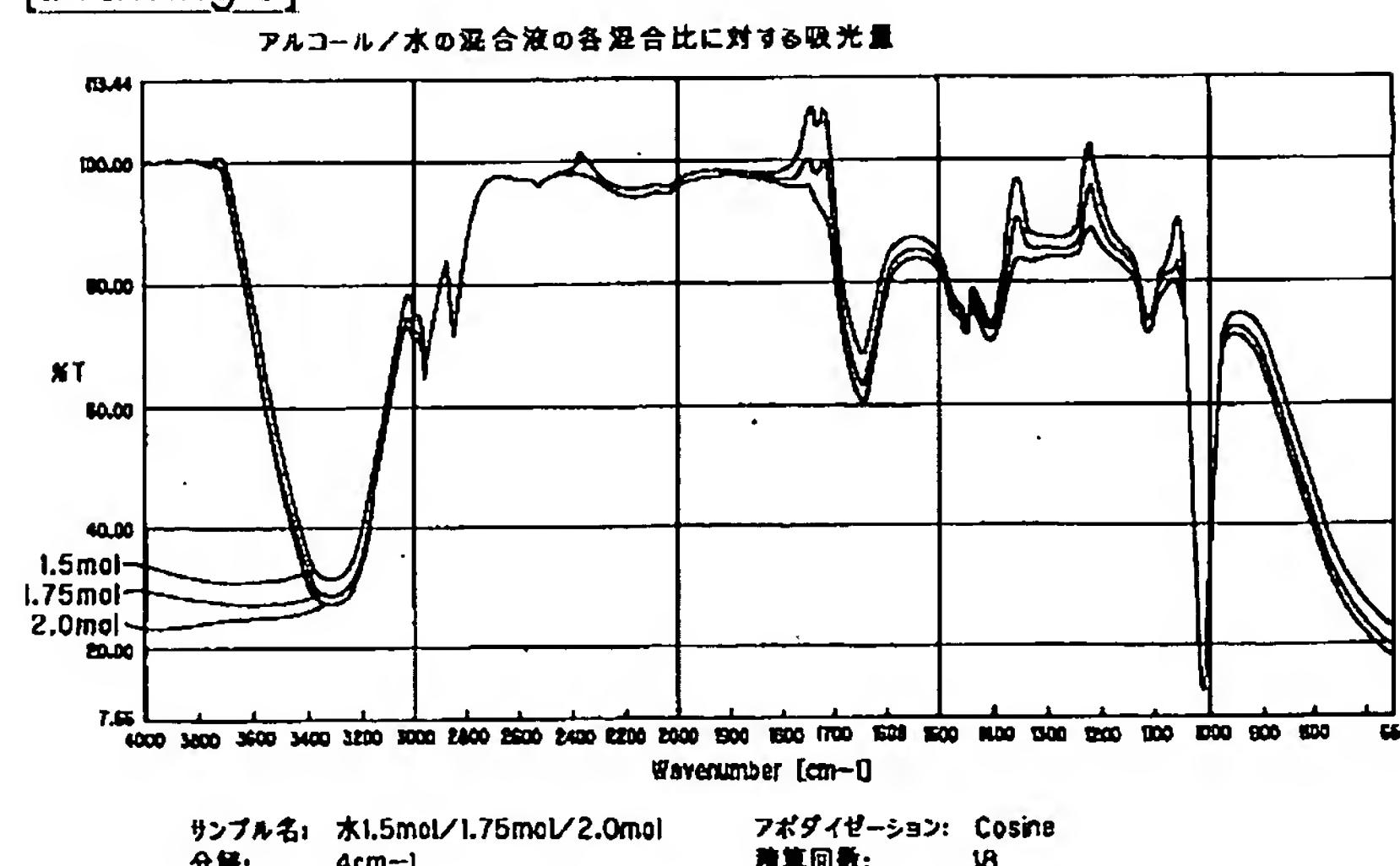


[Drawing 3]

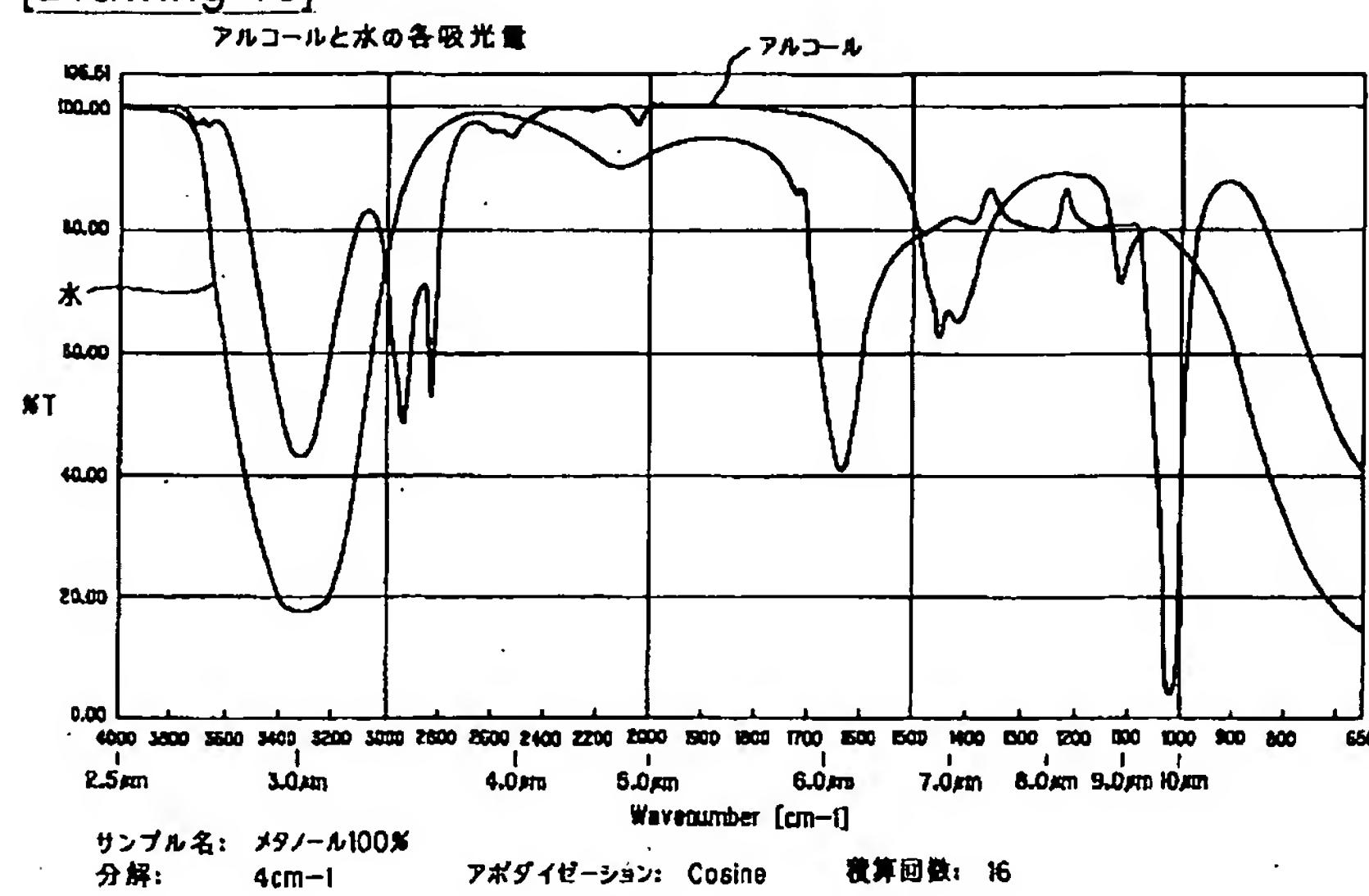


[Drawing 4]



[Drawing 5][Drawing 6][Drawing 7][Drawing 8][Drawing 9]

[Drawing 10]



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